UDC 666.263.2:666.1.038.8

CAPACITY OF GRANITOID-BASED GLASSES FOR GLASS CERAMICS FORMATION

S. E. Barantseva,[1] N. M. Bobkova,[1] V. G. Lugin,[1] and V. M. Kononovich[1]

Translated from Steklo i Keramika, No. 7, pp. 9 – 12, July, 2004.

The ability to form glass ceramics in glasses based on granitoids from the Republic of Belarus, which are a new type of petrological material for the silicate industry, is investigated. The concepts of the crystallization mechanism in glasses produced from mineral melts are formulated. It is established that the crystallization of the pyroxene phase proceeds according to the spherulite type on the stable chromium-picotite phase that is formed in glass cooling and persists up to the end of glass ceramics formation.

In view of the current problems faced by the contemporary science of materials, stricter environmental requirements, and the need to utilize industrial waste, interest in chemical and wear-resistant glass ceramic materials based on petrological resources is growing.

The operation of the Mikashevichskoe building stone deposit in the Republic of Belarus revealed an urgent need to utilize mineral rock screenings generated in the production of road gravel. The mineral rocks of this region include several varieties of which the prevalent ones are granitoids from the Mikashevichskoe lower Proterozoic complex represented by a series of magmatic rocks from diorites to leucogranites.

Our previous studies in the synthesis of petroglass ceramics and stone casting based on metadiabases [1, 2] demonstrated the possibility of using them for the production of chemically and wear-resistant glass ceramics. These properties are ensured by the formation of diopside-based pyroxenes and their solid solutions in crystallization [3].

In view of the difficulty of selective mining of metadiabases related to their specific bedding and the structure of the crystalline foundation, we investigated the possibility of using homogenized rocks representing a mixture of diorites, granodiorites, metadiabases, and granites for the production of glass ceramics, such as petroglass ceramics and stone casting. This mixture of mineral rocks is as close as possible to the real composition of screenings generated in the production of road gravel in the Mikashevichskoe quarry.

It is known that due to the wide isomorphism in chain silicates and the ease of formation of a continuous series of solid solutions between pyroxenes [4], the bounds of the content of main oxides in the production of pyroxene glass ceramics may vary within rather wide limits (up to ± 5 – 7 wt.%), which does not prevent active crystallization of pyroxene solid solutions.

Based on the studies of natural minerals [4 – 6], one of the theoretical reasons in designing pyroxene glass ceramics is the fact that aluminum-oxygen tetrahedra are capable of participating in the construction of complex polymerized structures only together with silicon-oxygen tetrahedra, the aluminum-oxygen tetrahedra being the weak units in these structures. Ribbon and chain structures may contain up to 25% aluminum-oxygen tetrahedra; in ring structures the latter can exist only in large rings, whereas isolated aluminum-oxygen tetrahedrons are not found in any natural mineral.

Thus, the whole range of polymer structures (from a skeleton to an isolated tetrahedron) is determined by the ratio O : Si = 2 – 4, and the crystallochemical parameter R = O : Si (the oxygen number) to a certain extent reflects the type of the structure. For chain silicates it is equal to 3 [5, 6].

Taking into account the possibility of up to 25% aluminum-oxygen tetrahedra being present in chain structures, we used the following expression to calculate the oxygen number:

$$R = \mathrm{O/Si} + 0.25\mathrm{Al}.$$

Table 1 lists the chemical compositions of granitoids from the south of Belarus and calculated compositions of granitoid-based experimental glasses.

Small quantities of impurity components from the initial material (P_2O_5, MnO, SO_3) similarly to the main stimulator (Cr_2O_3) can have an additional effect on the crystallization process, intensifying it and causing the formation of microheterogeneities in liquation separation.

The estimated oxygen number for synthesized glasses is 2.7 – 3.0. Consequently, the expected phase composition of glass ceramics should be represented by minerals of the pyroxene series with a chain structural pattern.

[1] Belarus State Technological University, Minsk, Belarus.

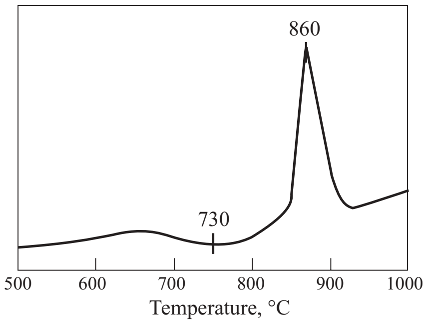

Fig. 1. Thermogram of glass SG.

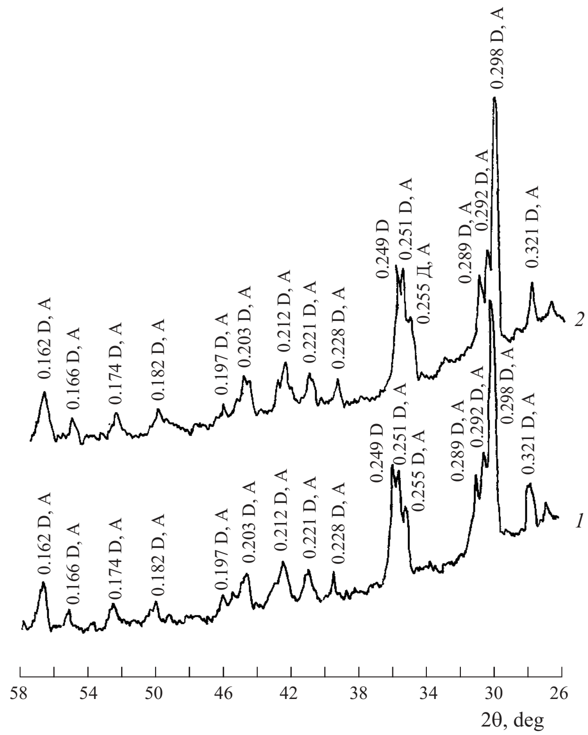

Fig. 2. Diffraction patterns of stone casting (*1*) and petroglass ceramic (*2*) obtained from glass SG: D) diopside, aluminodiopside; A) aluminoaugite.

The glass SG synthesized from the specified material mixture of granitoids and additives was used to analyze the technological characteristics of the melt and the glass, its crystallization capacity, and the possibility of producing glass-ceramic samples using different techniques.

The temperature of the synthesis of glass is 1440 – 1450°C, and the working temperature is 1210 – 1250°C. The crystallization capacity was studied using the gradient crystallization method in the temperature interval of 600 – 1000°C and the differential-thermal analysis in the temperature interval of 20 – 1000°C. It was found that the temperature interval of glass crystallization is quite wide (700 – 1000°C), and a close-crystalline devitrified structure with a dull fracture is formed at 800 – 1000°C, which indicates a substantial degree of crystallinity and a relatively small quantity of residual glass.

The DTA data are in full accordance with the results of gradient crystallization (Fig. 1). The main and the only maximum of the exothermic effect corresponding to the crystallization of the main phase is observed at 860°C. The surface area of the exothermic peak and its height point to an intense formation of the crystalline phase within the temperature interval of 800 – 900°C.

According to the DTA curve, the softening of glass occurs at temperatures of 670 – 750°C, which is an important criterion for the selection of the first stage of heat treatment when producing petroglass ceramics according to the two-stage crystallization schedule.

Based on experimental data it was found that the synthesis of glass ceramics is possible both by the pyroceram technology and by stone casting. To obtain a petroglass ceramic, the following two-stage heat-treatment schedule is recommended: 650°C for 1 h and 840 – 850°C for 1 h, and rate of the temperature rise 250 K/h. Petroglass ceramics can be obtain as well under single-stage thermal treatment for 2 h at a temperature of 800 – 850°C. When using the stone-casting technology (crystallization from “above”), 1-h exposure at 810 – 820°C is sufficient, and no propensity for deformation is observed in these samples.

The x-ray phase analysis of the glass-ceramics materials (Fig. 2) showed their phase composition (according to JCPDS data) to be identical and represented by the pyroxene solid solution of diopside $CaMg(SiO_3)_2$ with the crystal lattice parameters 0.238, 0.289, 0.255, 0.212, 0.196, and 0.166 nm; aluminodiopside $Ca(Mg, Fe, Al)(Si, Al)_2O_6$ with the lattice parameters 0.335, 0.298, 0.289, 0.255, 0.212, 0.197, 0.174, 0.150, and 0.141 nm and aluminoaugite $Ca(Mg, Fe^{3+}, Al)(Si, Al)_2O_6$ with the lattice parameters 0.334, 0.290, 0.289, 0.256, 0.212, 0.196, 0.174, and 0.150 nm. According to the x-ray phase analysis data, the conventional content of these minerals is 71.4, 15.3, and 9.1%, respectively.

TABLE 1

Material	Mass content, %							
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3 + FeO	MgO	CaO	Na_2O + K_2O	Cr_2O_3
Granitoids	54.10 – 75.69	0.19 – 1.17	12.64 – 17.00	1.32 – 9.77	0.30 – 4.27	0.93 – 6.83	4.93 – 8.37	Traces
Glass*	52.90 – 61.40	0.60 – 0.90	12.74 – 14.50	5.41 – 7.47	1.54 – 6.52	3.65 – 8.51	10.94 – 12.08	1.00

* Estimated compositions.

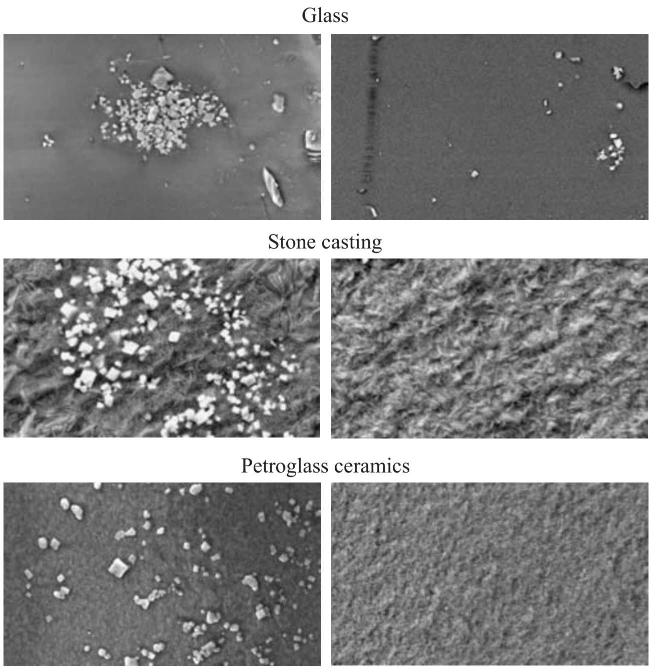

Fig. 3. Electron microscopes photos of the surface of various sites of fractures.

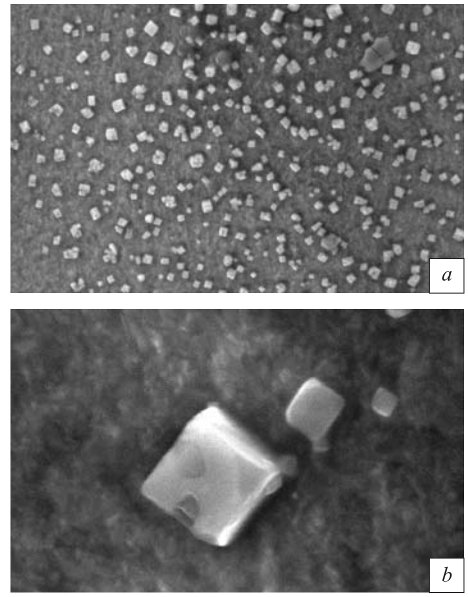

Fig. 4. Electron microscope photos of the surface of a petroglass ceramic fracture with magnification × 2000 (*a*) and × 10,000 (*b*).

The study of the microstructure of glass and glass ceramics based on this glass was performed using a JEOL JSM-5610LV scanning electron microscope equipped with the system of electron-probe energy-dispersion chemical analysis JED-2201 allowing for quantitative and qualitative analysis of the whole matrix and its local zones.

The electron microscope studies were performed in low vacuum using a detector of reverse-reflected electrons, which made it possible to obtain an image of the sample surface without applying conductive coatings.

It is widely believed [3] that the process of pyroxene formation is related to the formation of a metastable chromium-spinelide phase in glass at the first stage of heat treatment (650 – 750°C), which actively promotes the crystallization of pyroxenes under a further increase in the heat treatment temperature and exposure at the optimum temperature corresponding to the exothermic maximum on the DTA curves.

Different sites of the same surface fracture were analyzed, which revealed the nature of the distribution of emerging crystalline phases (Fig. 3).

Spinelides emerge in cooling of the mineral melts considered and are clearly visible on the surface of the hardened glass fracture. Chromium-spinelide formations constitute aggregates with different concentrations of crystals with cubic syngony and crystals approaching the hexahedral shape randomly dispersed over the whole field. A similar picture is observed in the crystallized samples of stone casting and petroglass ceramics, which differ only in the type of their structure, more coarse-crystalline in the former and finely crystalline in the latter.

The electron-microscope photos of the surface of a petroglass ceramic fracture (Fig. 4) clearly exhibit a rather homogeneous distribution of single chromium-spinelide crystals of cubic syngony with magnification × 2000, and when the same site is magnified × 10,000, hexahedral crystal of different sizes (from 0.5 to 3.0 μm) corresponding to chromium spinelides in their habitus are clearly visible.

The qualitative and quantitative microprobe analysis of crystalline inclusions in glass and crystallized samples of stone casting and petroglass ceramics indicates that their compositions are identical (wt.%): 11.0 – 14.0 MgO, 10.0 – 12.0 FeO, 12.0 – 13.5 Al_2O_3, 38.0 – 44.0 Cr_2O_3, i.e., they constitute aluminochromium-spinelides. A similar analysis of local sites of the matrix established the following composition (%): 58 – 59 SiO_2, 11 – 12 MgO, 8 – 9 CaO, 17 – 19 Al_2O_3, and 5 – 6 FeO. This determines the formation of pyroxene solid solutions, the chromium oxide being completely incorporated into chromium-spinelides.

Consequently, the chromium-spinelide formed in glass cooling corresponds to the composition of chromium-picotite $(Mg, Fe)(Cr, Al)_2O_4$, which is preserved in the course of devitrification up to the formation of a pyroceramic structure.

The growth of the pyroxene crystal phase on chromium-picotite formations proceeds according to the spherulite type by means of nucleation of radial-radiant needle-shaped crystals and their interweaving of different patterns, which is clearly seen in Fig. 3 (stone casting).

It is known that the group growth of spherulites obeys the law of geometric selection; the final structure of the aggregate is created by spherulites growing to large sizes, whereas other spherulites stop their growth for lack of space.

The general structure of crystallized stone-casting samples and petroglass ceramics is typical of chain pyroxenes with the preserved stable chromium-spinelide phase that is formed in cooling of the mineral melt.

The chemical resistance of petroglass ceramics to 1 N HCl is 99.68 – 99.87%, its microhardness is 7000 – 7500 MPa, and the wear-resistance coefficient of stone-cast samples is 0.052 %/h, which makes them applicable for multifunctional uses as lining materials in aggressive media and as milling bodies in milling different materials and parts operating under various types of friction.

Thus, the use of granitoids from the Mikashevichskoe deposit for the production of glass ceramics (petrogass ceramics and stone casting) will make it possible to expand the list of available raw materials for silicate production and to decrease import of products from Ukraine.

REFERENCES

1. N. M. Bobkova, S. E. Barantseva, and A. I. Galaburda, "Production of wear-resistant petroglass ceramics based on diabases from the Republic of Belarus," *Vestsi Nats. Akad. Navuk B, Ser. Khim. Navuk*, No. 1, 92 – 95 (2002).
2. S. E. Barantseva, "Wear-resistant stone casting based on diabases from Belarus," *Prom. Bezopasnost'*, No. 1, 43 – 44 (2001).
3. L. A. Zhunina, M. I. Kuz'menkov, and V. N. Yaglov, *Pyroxene Glass Ceramics* [in Russian], BGU, Minsk (1974).
4. W. Deer, R. Howie, and J. Zusman, *Rock-Forming Minerals, Vol. 2, Chain Silicates*, London (1963).
5. N. A. Toropov and L. N. Bulak, *Crystallography and Mineralogy* [in Russian], Stroiizdat, Leningrad (1972).
6. H. Batty and A. Pring, *Mineralogy for Students* [Russian translation], Mir, Moscow (2001).